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Characterization and Performance Evaluation of PDMS/PSF Membrane for CO_2/CH_4 Separation under the Effect of Swelling

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Abstract

In this work, Polydimethyl siloxane/polysulfone (PDMS/PSF) membrane was developed by dip coating of developed PSF membrane. Developed membranes were characterized in terms of thermal analysis, glass transition temperature, and membrane morphology. Performances of the developed membranes were tested using gas permeation equipment within the pressure range of 2-10 bar. To study the water swelling in membrane, developed membranes were soaked in distilled water for 5 minutes. Gas permeation in membrane was investigated before and after swelling. Based on the results, increase in CO_2 permeance was observed due to plasticization in membrane before swelling. However, CO_2 permeance decreased after swelling in membrane. Swelling affected the separation performance of membrane by decreasing its permeance. While, CO_2/CH_4 selectivity has increased after membrane swelled. Hence, swelling resulted in membrane contraction, which contributed to the increase of selectivity. Pure polysulfone membrane exhibited higher degree of swelling, whereas PDMS/PSF membranes demonstrated substantial high resistance toward swelling. Based on swelling degree of PDMS/PSF composite membrane, this membrane can be considered as a potential water (swelling) resistant polymeric membrane for CO_2/CH_4 separation.

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Keywords: CO_2/CH_4 separation; Swelling; Permeance; Selectivity

1. Introduction

Natural gas is one of the important and primary sources of energy. Natural gas reserves are contaminated with high percentages of CO_2. Purification of natural gas is necessary to meet pipeline specifications and to use it on

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domestic and commercial scale Major constituent of natural gas is methane with the composition range of 30-90 mol%[1]. Different technologies are used for natural gas processing and purification. Natural gas processing includes adsorption, absorption, cryogenic distillation and membrane process. All these processes face some limitations in terms of high cost and complexity in process[2].

Membrane technology is one of the most emerging techniques used for natural gas purification. The main advantage of membrane separation is a simple and economical process without any major limitations. Membrane process offers up to 90% separation efficiency in a very minimal cost. Different types of membranes are used in natural gas purification[3]. These types include inorganic membranes, mixed matrix membranes and polymeric membranes. Polymeric membranes are widely used in gas separation applications due to excellent separation performance. Moreover, variety of polymeric materials can be used as a membrane in gas separation applications. Polymeric membranes are best candidate to be used under aggressive feed conditions due to their modular nature[3, 4]. Performance of the polymeric membranes is affected by plasticization and swelling in membrane. Swelling is caused by the presence of humidity in feed gas. Membrane swelling results in the deformation of polymer structure and consequently it affects the separation performance of membrane by decreasing the separation factor [5, 6]. In this work, effect of swelling on separation performance of membrane was studied.

Composite membrane is one of the types of polymeric membrane. Composite membrane is a dual layer membrane with porous support and selective top layer. Composite membrane is a potential membrane to be used in harsh operating conditions due to its excellent mechanical strength [7]. Dip coating and manual film casting techniques are used to develop composite membrane. Natural gas separation through composite polymeric membrane has been reported in literature by many researchers. Shamsabadi et al. [8] investigated gas separation in polydimethyl siloxane/polyetherimide (PDMS/PEI) composite membrane developed by dip coating and solution casting. Membranes developed by dip coating showed better separation performance in case of H_2/CH_4 mixed gas. Mansoori et al.[9] prepared a polydimethyl siloxane/polysulfone (PDMS/PSF) membrane and reported the CO_2/CH_4 selectivity of 39.81 at the feed pressure of 10 bar. Sadrzadeh et al.[10] synthesized polydimethyl siloxane/polyether sulfone (PDMS/PES) composite membrane and investigated the gas permeation of CO_2, CH_4 and H_2 in developed composite membrane. Madaeni et al.[7] studied the effect of coating method on the separation performance of PDMS/PES composite membrane. Composite membrane was developed by dip coating and solution casting method.

In present work, polydimethyl siloxane/polysulfone (PDMS/PSF) membrane was developed by dip coating of PSF with PDMS. PDMS is a rubbery polymer having excellent permeability in gas separation with super hydrophobic characteristics. PDMS also exhibits excellent mechanical and chemical stability [7]. PSF is a glassy polymer with excellent separation performance in CO_2 separation [11]. The main purpose of this work was to investigate the gas separation performance of PDMS/PSF membrane under the effect of water swelling in membrane. Gas permeation properties of PDMS/PSF membrane were reported in literature by some researchers but the effect of membrane swelling on separation performance was not investigated.

Nomenclature

P/l	Permeance of any species in GPU
l	Membrane Thickness
j	Flux of the specific species
ΔP	Partial Pressure across the membrane
GPU	Gas Permeance Unit
PDMS	Polydimethyl Siloxane
PSF	Polysulfone
PDMS/PSF (60, 120 & 180)	PDMS/PSF membrane with coating time of 60, 120 & 180 minutes

2. Experimental Method

2.1. Materials & Chemicals

Polysulfone (PSF) Udel® 1800 was purchased from Solvay Advanced Polymers Inc. U.S. Polysulfone was in powder form and dried for 24 hours before use. Polydimethyl Siloxane (PDMS) was supplied by Acros Organics, Belgium. Solvents n-hexane and N-Methyl-2-pyrrolidone (NMP) were purchased from Merck. Pure carbon dioxide and methane used in gas permeation experiments were purchased from Gas Walker Sdn. Bhd.

2.2. Membrane Synthesis

First of all asymmetric polysulfone (PSF) membrane was developed by phase inversion technique. A homogeneous casting solution of PSF was obtained by adding 20 wt. % of PSF in NMP followed by continuous stirring of 24 hours at room temperature. After that this casting solution was degassed for 4 hours using ultra sonication bath to remove the bubbles from the solution. After degassing the homogeneous casting solution was kept at room temperature for 12 hours. Membranes were casted on glass plate using casting knife with the opening of 25 microns. For precipitation step, casted membranes were placed in deionized water for 24 hours. After 24 hours, membranes were peeled off from glass plate and kept for atmospheric drying for 12 hours. To completely remove the residual water content, membranes were dried overnight in vacuum oven at 80 ^{0}C.

2.3. Composite Membrane Preparation

Composite membrane was developed by modification of developed polysulfone membrane. Dip coating was used to prepare composite membrane. Developed polysulfone membranes were immersed in PDMS solution for different time periods. PDMS solution was prepared by adding 20 wt. % PDMS in solvent. *n*-hexane was used as a solvent for this purpose. After gentle stirring a homogeneous coating solution of PDMS was obtained. Synthesized polysulfone (PSF) membranes were immersed in this coating solution for 60, 120 & 180 minutes. After dip coating of PSF membranes, the additional solution was removed from the surface of the membrane. Modified membranes were subjected to thermal treatment for 30 minutes at 120 ^{0}C. After complete crosslinking of PDMS with PSF, PDMS/PSF membrane was cured.

2.4. Swelling Experiments

For the developed PSF and PDMS/PSF composite membrane, swelling experiments were performed by soaking all the developed membrane samples in distilled water for 5 minutes at atmospheric conditions. This method was used by Kelman et al. [12] to study the solvent swelling in membrane. Water uptake of membrane in 5 minutes was defined by degree of swelling. Degree of swelling was calculated by the equation reported by Deng et al. [6]. All the membrane samples were cut according to the diameter (1.98 cm) of the permeation test cell. Weight of the swollen wet membrane and dry membrane was noted and degree of swelling was calculated by the equation given below.

$$\frac{w_2 - w_1}{w_1} \times 100 \tag{1}$$

Whereby, w_2 is the weight of wet membrane and w_1 is the weight of dry membrane before swelling.

2.5. Characterization

Synthesized PDMS/PSF membrane was characterized in terms of thermal stability, glass transition temperature, morphology and functional groups study using thermo gravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and FESEM (Field emission scanning electron microscopy).

2.6. Permeation tests

Performance of the developed membranes was evaluated by testing the permeation of pure carbon dioxide and methane within the pressure ranges of 2-10 bar at room temperature. Permeation tests were performed under two conditions which are before membrane swelling and after membrane swelling. Results were compared to study the effect of membrane swelling on separation performance of developed membranes.

Permeation tests were performed in gas permeation equipment with the membrane test cell having effective surface area of 3.14 cm^2. The permeation equipment used in this study was described in detail by Jusoh et al. [13]. Permeance for carbon dioxide and methane was calculated by the following equation.

$$\frac{P}{l} = \frac{j}{\Delta P} \tag{2}$$

Where, P/l is the permeance of specific species, j is the flux of the species and ΔP is the partial pressure of particular species across the membrane and l is the thickness of the membrane. CO_2/CH_4 ideal selectivity was calculated by taking the ratio of CO_2 & CH_4 permeance. Permeance and selectivity values before and after swelling were compared to study the effect of swelling on separation performance of membrane.

3. Results and Discussions

3.1. Degree of Swelling (SD %)

Degree of swelling defines the water uptake of membrane. Swelling degree value indicates that swelling in PDMS/PSF composite membrane decreases with increasing PDMS coating time. In case of pure PSF membrane, swelling degree was calculated as 134.17%. The value of swelling degree was very high indicating that complete swelling occurred in PSF membrane. However, in PDMS/PSF composite membrane with immersion time of 60 minutes, the swelling degree was calculated as 19.36 %. As compared to pure PSF membrane the swelling degree of PDMS/PSF membrane was very low. The reason of low swelling degree in composite membrane attributes to the highly water resistant (hydrophobic) nature of PDMS. Swelling degree in PDMS/PSF membrane samples with coating time of 120 and 180 minutes was calculated as 16.72% and 14.34% respectively. Swelling degree values indicate that developed PDMS/PSF membrane has a potential to resist water swelling.

3.2. Characterization

3.2.1. Thermo gravimetric Analysis (TGA) & Differential Scanning Calorimetry (DSC)

Thermal analysis of developed membranes was carried out using TGA. Fig. 1(a) shows the TGA curves for PSF membrane and PDMS/PSF membranes.

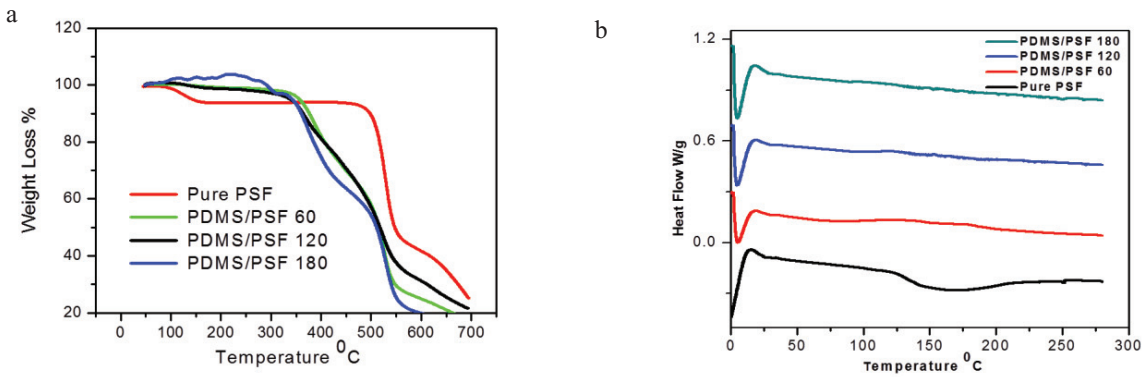

Fig. 1. (a) TGA Curves of developed membrane samples (b) DSC thermo grams for developed membranes

Based on fig. 1 (a), TGA results for all the membrane samples are as per expectations because increase in temperature loses the intermolecular chains between the polymer molecules in polymeric membrane, resulting a decrement in the mechanical and thermal strength of polymer. TGA curve of pure untreated PSF membrane show two different inflections indicating weight loss at two different points. Weight loss started at temperature above 100 ^{0}C. This indicates the presence of small traces of solvent or moisture in PSF membrane. PSF membrane showed excellent thermal stability up to the temperature of 500 ^{0}C. After 500 ^{0}C sample start decomposing and huge decrease in weight loss was observed. Thermal degradation temperature for pure polysulfone membrane was 505.80 ^{0}C. Weight loss curve of PDMS/PSF 60 membrane show single weight loss inflection. No Weight loss was observed between 100-200 ^{0}C which indicates that this sample is free from moisture completely. Thermal degradation temperature for composite membrane was found to be 455.34 ^{0}C. Degradation temperature of composite membrane was less than pure PSF membrane. The reason behind this is the poor thermal stability of PDMS [7]. So, the addition of PDMS affected the thermal stability of PSF. PDMS/PSF 120 also have a single weight loss inflection showing single degradation temperature. Sample decomposition started between 300-400 ^{0}C and degradation temperature was observed as 424.18 ^{0}C. Degradation temperature of composite membrane immersed for 120 minutes is less than that of membrane immersed for 60 minutes. As immersion time was doubled for this membrane so there was more contact between PDMS solution and PSF membrane, thus highly affecting the thermal stability of membrane. PDMS/PSF 180 membrane show various inflections which indicate the presence of solvent in membrane. First weight loss was observed at 150 ^{0}C, indicating the traces of moisture in membrane. Weight loss was also observed at 290 ^{0}C due to the presence of residual solvent in the sample [13]. This can be eliminated by increasing the drying time of membrane so that the residual solvent and moisture dries completely. Sample starts decomposing between 300-400 ^{0}C and degradation temperature was observed as 446.65 ^{0}C. Degradation temperature of all the prepared membrane samples was found to be reasonable for gas separation applications. It can also be concluded that immersion time in dip coating method affects the thermal stability of the composite membrane.

Fig. 1 (b) shows the DSC thermo grams for developed membranes. In case of pure polysulfone membrane the temperature versus heat flow curve indicate single glass transition temperature Tg. Tg for PSF membrane was observed between 180-190 ^{0}C, which is in line with the characteristic Tg value (185 ^{0}C) for polysulfone [14]. PDMS/PSF membrane with the immersion time of 60 minutes (PDMS/PSF 60) has variation in DSC thermo gram at two different points. Thus, this membrane sample does not exhibit single Tg value. First transition point was observed between 60-90 ^{0}C, while second variation in peak occurred at 170 ^{0}C. Second value is close to the characteristic Tg value of PSF, while this change in glass transition temperature of composite membrane was due to PDMS. PDMS is one of the polymer with lowest Tg (-125^{0}C) values. Thus, it can be predicted that the addition of PDMS to PSF affected the glass transition temperature of pure polysulfone. DSC thermo gram of PDMS/PSF composite membrane with immersion time of 120 minutes PDMS/PSF 120 also shows two different Tg values. Similarly, PDMS/PSF 180 show different Tg values. From the DSC results, it was concluded that addition of PDMS affect the glass transition temperature of polysulfone membrane by lowering the Tg values.

3.2.2 Field Emission Scanning Electron Microscopy (FESEM)

Fig. 2 (a-d) shows the cross sectional FESEM images for developed membranes. Fig. 2 (a) represents the pure polysulfone membrane. Cross section of pure polysulfone membrane shows the porous structure of membrane with variation in the pore sizes. Sponge type porous structure was observed in polysulfone membrane. Fig. 2(b) shows the cross sectional morphology of PDMS/PSF 60 membrane. Cross section of developed composite membrane was observed to be different from pure polysulfone membrane, which indicates the change in the molecular structure due to modification of polysulfone membrane. Finger like or tear like pores were observed in cross section of composite membrane. Cross section of composite membrane was found to be in accordance with the literature reported [8, 10, 15, 16]. SEM results of composite membrane. Almost for all types of composite membranes finger like pores were observed in cross section. Some macro voids were observed in cross section of PDMS/PSF 60 composite membrane (fig.2-b). Phase inversion kinetics play an important role in formation of macro voids and poor phase mixing might be the possible reason for formation of macro voids in the structure of membrane.

Fig. 2(c) shows the cross section FESEM image of PDMS/PSF membrane with immersion time of 120 minutes (PDMS/PSF 120). Similar finger or tear type pores were observed in cross section of PDMS/PSF 120 composite membrane. No macro voids were observed for this membrane sample. Fig. 2(d) shows the cross section of PDMS/PSF composite membrane having immersion time of 180 minutes (PDMS/PSF 180). Similar cross section was observed with finger layered pores and very few macro voids in membrane micro structure.

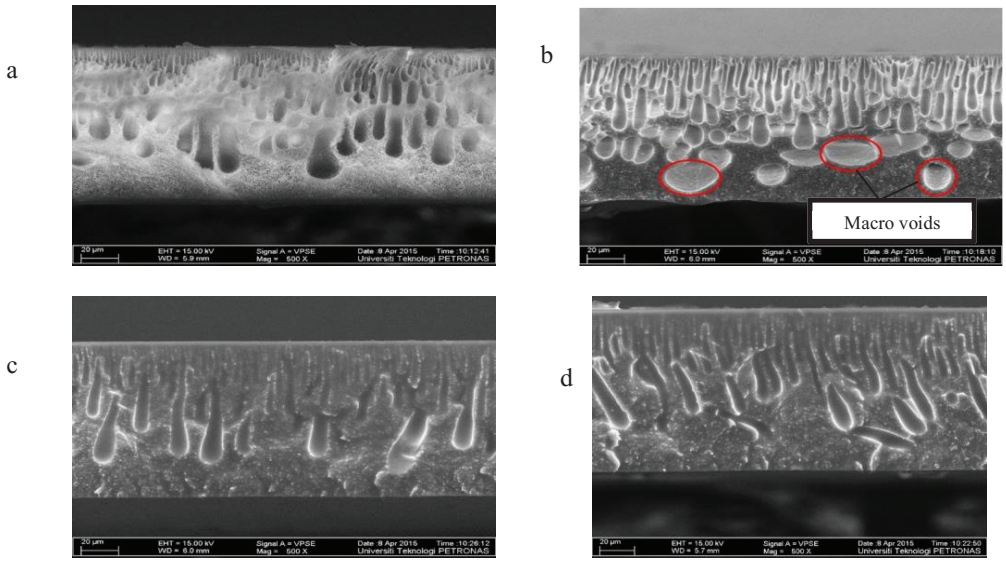

Fig. 2. Cross sectional FESEM images of (a) Pure polysulfone membrane (b) PDMS/PSF 60 membrane (c) PDMS/PSF 120 membrane (d) PDMS/PSF 180 membrane.

3.3. Permeation Results

Permeation tests were performed before and after swelling in membrane for all the developed membrane samples. Results were compared to study the effect of swelling on performance of developed membrane. Fig. 3 (a) shows the CO_2 permeance for developed composite membrane samples with respect to change in feed pressure.

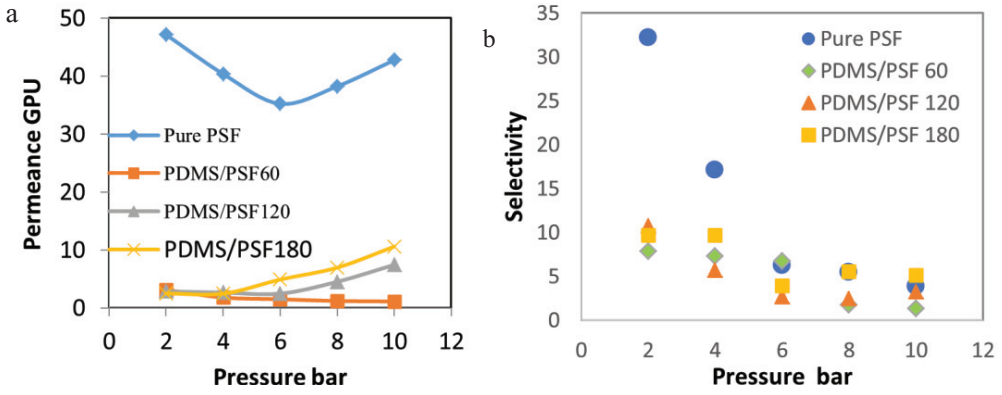

Fig.3. (a) CO_2 permeance and (b) CO_2/CH_4 selectivity for all the developed membranes before swelling

It was observed that generally CO_2 permeance decreased with increasing pressure for all the membrane samples before swelling. But after pressure of 6 bar sudden increase in permeance was observed for PSF, PDMS/PSF 120 and PDMS/PSF 180. This increase in permeance indicates that plasticization occurred at 6 bar for all these

membrane samples. Plasticization results in the increase in membrane free volume, thus causing high permeation and diffusion of the penetrant gas. Plasticization results in high permeability of gases, but a destructive decrease in separation factor of membrane. However, for PDMS/PSF 60 membrane, no plasticization phenomenon was observed because permeance decreased with increasing pressure steadily. Decrease in CO_2 permeance with increasing pressure is in agreement with dual sorption behaviour of glassy polymers [15, 16].

Fig. 3 (b) shows the CO_2/CH_4 selectivity for all the membrane samples before swelling. It was observed that selectivity decreases with increasing pressure for all membrane samples. The main reason of decrement in selectivity values was plasticization in membrane [17]. As plasticization was observed during CO_2 and CH_4 permeance, this plasticization caused decrease in selectivity values for all the membrane samples.

After membrane swelling, CO_2 permeance increases with increasing pressure (Fig. 4 a). It was observed that after 6 bar CO_2 permeance start increasing with increasing pressure. Fig. 4 (a) shows the change in CO_2 permeance with increasing pressure. CO_2 permeance of pure polysulfone membrane was 3.78 GPU and 4.25 GPU at 2 and 4 bar respectively. At 8 bar, two fold increase in CO_2 permeance was observed indicating that membrane plasticizes at this pressure. PDMS/PSF 60 composite membrane also show increase in CO_2 permeance with increasing pressure. Increase in permeance started after 6 bar feed pressure. Permeance value at 6 bar was 4.09 GPU, 10% increase in permeance was observed at 8 bar for this composite membrane sample. PDMS/PSF 120 composite membrane exhibits the similar behavior as PDMS/PSF 60. Thus, for CO_2 permeance, in all the membrane samples permeance was observed to increase at 8 bar. Hence, 8 bar is termed as the plasticization pressure in case of CO_2 permeance for developed composite membrane.

CO_2/CH_4 selectivity was increasing with increasing pressure for all the developed membranes after swelling (Fig.4 b). This indicates that there is no plasticization effect in membrane after water swelling. In case of PDMS/PSF 180, selectivity increases with increasing pressure. The selectivity values were very high as compared to the selectivity values of same membrane before swelling. For example, before swelling the maximum selectivity at 10 bar for PDMS/PSF 180 was 5.10, but after swelling unexpected increase in selectivity was observed. After swelling, selectivity at 10 bar for PDMS/PSF membrane was 85. The high selectivity value indicates that water swelling in membrane caused contraction in membrane pores, due to which selectivity was increased dramatically.

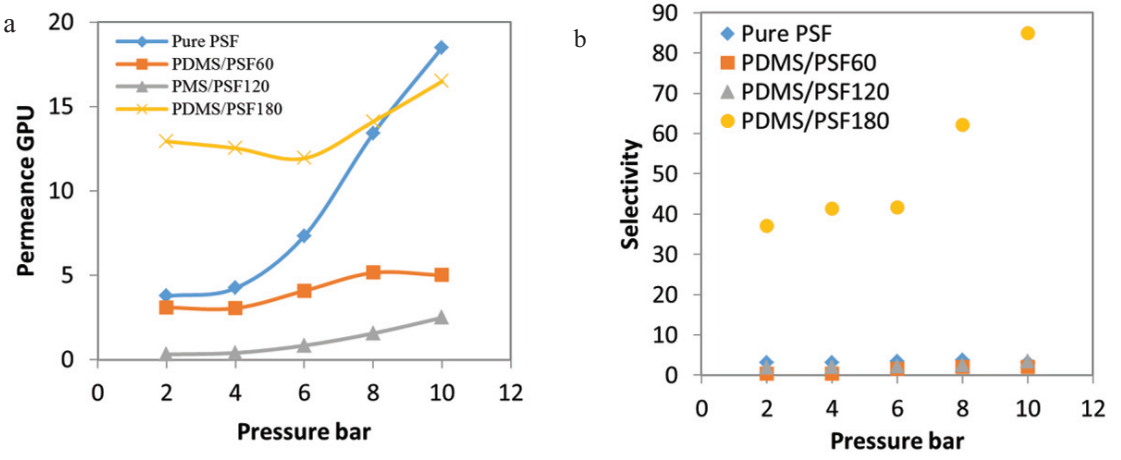

Fig.4. (a) CO_2 permeance and (b) CO_2/CH_4 Selectivity of developed membranes after swelling

4. Conclusions

PDMS/PSF composite membrane with different PDMS coating times (60, 120 and 180 minutes) was developed by using dip coating method. TGA results indicate decrease in thermal stability of membrane with increasing temperature. Moreover, pure polysulfone membrane was thermally more stable than composite membrane with

higher thermal degradation temperature. PDMS coating affected the thermal stability of the membrane. DSC results reveal that only pure polysulfone membrane have single glass transition temperature (Tg). PDMS coating resulted in more than one glass transition temperature values for composite membrane samples. FESEM results reveal that all the membrane samples have dense top layer supported by the porous layer. Sponge type structure was observed in morphology of pure polysulfone membrane, while finger or tear like sub layers were observed in morphology of composite membrane samples. In permeation analysis before membrane swelling, CO_2 permeance was observed to increase at certain pressures indicating plasticization in membrane at that particular pressure. Decrement in CO_2/CH_4 selectivity was also attributed to the plasticization in membrane. CO_2/CH_4 selectivity was observed to increase after membrane swelling. Based on degree of swelling values, PDMS/PSF membrane has a potential to be utilized as a water (swelling) resistant polymeric membrane for CO_2/CH_4 separation.

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